The structure relaxation of carbon nanotube

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(February 1, 2008)

Abstract

A simple macroscopic continuum elasticity theory (CET) is used to calculate the structure relaxation of single-wall carbon nanotube (SWNT), an analytic formula is obtained. We also expand an atomic scale three-parameter empirical model [T. Lenosky *et* al. Nature 355, 333(1992)] in order to correctly describe the bond-length change effects. The structure relaxation of SWNT expected by the model is good in agreement with our CET results, and very well consistent with the previous calculation from a first principles local density function approximation. Using the expanded Lenosky model, we calculate the strain energy of bending tube. The obtained results are good in agreement with the previous theoretical expectation. It shows the model may be a good simple replacement of some more sophisticated methods on determining carbon networks deformations.

PACS : 61.46. +w, 61.48.+c, 63.20.Dj
Keywords: carbon nanotube, structure relaxation, elasticity theory, the expanded Lenosky model

Recently, carbon nanotubes with cylindrical graphite structures have been intensively investigated [1], and many experimental and theoretical researches have been performed [2–5]. The structure of nanotubes is qualitatively well known through the simple construction of rolling a perfect graphene sheet, where only one parameter is to be determined: The lattice parameter or a bond-length. The first-principles local density function approximation (LDA) [6,7], tight-binding (TB) approximation [2] and empirical potential methods [8–11] have been used to determine the bond-length of tube. In all these theoretical studies, a small relaxation effect has been found, the bond length of tubes is not equal to that of graphene sheet since the curvature of the tubes and thus the structural inequivalence between the axis and normal direction render the carbon-atom hexagons distorted, although the details of the bond relaxation from different authors are different. In this letter, we use a simple macroscopic continuum elasticity theory (CET) and an expand microscopic empirical model to calculate the bond length relaxation of single-wall carbon nanotubes (SWNTs). We find from both the two methods: (1) the radius of any SWNT is slightly larger than the expected value from the rolling graphene sheet. (2) The radius relative increasing of SWNT is reverse proportion to the square of the tube radius, and independent or slightly dependent on the helicity of tubes. Our results are in good in agreement with the previous LDA results. (3)Although the energy contribution of bond-length change is very small in straight SWNT [12], it can strongly affect the structure relaxation of tubes. (4) We use the expand model to describe the bending of nanotube, and find the obtained results are good consistent with the previous theoretical expectation.

SWNT can be indexed by a pair of integers (n_1, n_2) [3]. From the rolling graphene model, we have

$$\rho_0 = \frac{\sqrt{(n_1^2 + n_1 \cdot n_2 + n_2^2)} \cdot a}{2\pi}, \tag{1}$$

where ρ_0 is the non-relaxed radius of SWNT, $a = \sqrt{3} r_0$ is the lattice constant of graphite sheet, $r_0 = 1.42\ \mathring{A}$ is the bond length of graphene. Supposing the relaxed radius is ρ, we define

$$\epsilon = \frac{\rho - \rho_0}{\rho_0}. \tag{2}$$

A number of theoretical and experimental studies show the deformations of graphenes and SWNTs can be well described by the CET [7,9,10,13,14]. The rolling energy of graphene is only dependent on the rolling radius, and the stretching energy is only dependent on the relative elongation, independent on the rolling and stretching direction of graphite sheet, and we have

$$E_r = C/\rho^2, \tag{3}$$

$$E_s = \frac{1}{2} E'' \cdot \epsilon^2. \tag{4}$$

Here E_r and E_s are the rolling and stretching energy per atom, respectively. $C \approx 1.2 \sim 2.0\ eV\mathring{A}^2$, depending on the different models, $E'' \approx 58 \sim 59\ eV$ [7,9,10,13,14]. When rolling a graphite sheet to SWNT, the bonds are stretched in the circumference direction of tube,

(we neglect the possible smaller strains in the axis direction). The strain energy per atom is the sums of the rolling and stretching energy.

$$E_t = \frac{1}{2}E'' \cdot \epsilon^2 + \frac{C}{{\rho_0}^2(1+\epsilon)^2} \tag{5}$$

Minimizing the strain energy, we obtain

$$\epsilon \approx \frac{2C}{E'' + 6C/{\rho_0}^2}\frac{1}{\rho_0^2} \approx \frac{2C}{E''}\frac{1}{{\rho_0}^2} \tag{6}$$

So we obtain, $\epsilon \approx \frac{0.05}{\rho_0^2}$, (selecting $C = 1.44\ eV\mathring{A}^2$ [14])where the unit of ρ_0 is $\mathring{A}$. The results show: (1) any tube is relaxed when it is rolled from graphite sheet and the relaxation is slight but obvious; It is consistent with the previous theoretical expection [2,6,7,15] (2) Although the stretching energy from the dilation of tube radius E_s is far smaller than the curvature energy contribution E_r, can be safely neglected [12,14], the size of the radius dilation ϵ is sensitively dependent on E_s.

For more carefully discuss the relaxation effects, we also consider a microscopic model. Lenosky *et* al. employed a three-parameter empirical model which can well describe the structure of the curved carbon networks while the bond lengths are constrained to r_0. Ou-Yang *et* al. [13] reduced the model to a two-elastic-modulus macroscopic continuous model and well treated the deformed energy of multi-wall carbon nanotube. However, for describing some deformations which the bond lengths are obvious changed, such as bending or stretching tube, we need a more complete model which must including the contribution from the bond length [12],

$$\begin{aligned} E_t = {} & \mathcal{E}_0 \sum_{(ij)} \frac{1}{2}(r_{ij} - r_0)^2 + \mathcal{E}_1 \sum_i (\sum_{(j)} \hat{u}_{ij})^2 \\ & + \mathcal{E}_2 \sum_{(ij)} (1 - \hat{n}_i \cdot \hat{n}_j) + \mathcal{E}_3 \sum_{(ij)} (\hat{n}_i \cdot \hat{u}_{ij})(\hat{n}_j \cdot \hat{u}_{ij}) \end{aligned} \tag{7}$$

where $\hat{u}_{ij}$ is a unit vector pointing from carbon atom i to its neighbor j, r_{ij} is the distance between the atom i and atom j, and $\hat{n}_i$ is a unit vector normal to the fullerene surface at atom i. The summation $\sum_{(j)}$ is taken over the three nearest neighbor j atoms on atom i, and the summation $\sum_{(ij)}$ is taken over only the nearest neighbor atom pairs. Supposing $r_{ij} = r_0$, fitting to LDA calculation, Lenosky obtained the values of ($\mathcal{E}_1$, $\mathcal{E}_2$, $\mathcal{E}_3$) which are $(0.96, 1.29, 0.05)\ eV$, respectively [12].

Using an empirical 4th-neighbor force-constant model of graphite [16], which has been well described the different deformation of both graphite and SWNT [10] and correctly calculated the elastic modulus, we can compute the strain energy of SWNTs with different deformations. Fitting the values of E'' and Poisson ratio σ of SWNT and graphite sheet which are calculated from the force-constant model, we obtain the value of $\mathcal{E}_0$ is 57 $eV/\mathring{A}^2$. Since the bond-length change of SWNT is determined by the first order derivative of energy rather than energy itself, although the first term energy of eq. (7) in straight SWNT is very small [12,14], the value of $\mathcal{E}_0$ still strongly affect the equilibrium structure of SWNT.

The carbon atom positions of SWNT can be located from the rolling graphene sheet [14], the vectors $\vec{u}_{ij}$ can be easily obtained,

$$\vec{u}_{ij} = (r_0 \sin\theta_{ij})\hat{e}_z - 2\rho_0 \sin^2\frac{\phi_{ij}}{2}\hat{e}_{r_i} + \rho_0 \sin\phi_{ij}\hat{e}_{\phi_i}, \tag{8}$$

where θ_{ij} is the angle between $\vec{u}_{ij}$ and the circumference direction. $\hat{e}_z$, $\hat{e}_{r_i}$ and $\hat{e}_{\phi_i}$ are the unit vectors of axis, radial and tangent direction at atom i, respectively. ϕ_{ij} is the relative azimuth between the atom i and the nearest neighbor atom j, independent on the site i, we have

$$\phi_{ij} = \frac{r_0 \cos\theta_{ij}}{\rho_0}. \tag{9}$$

After considering the relaxation effect, the radius and bond length will be stretched. $\vec{u}_{ij}$ is approximately obtained, if ρ_0 is replaced by the relaxed radius ρ, and ϕ_{ij} is not changed, where we have neglected the higher order terms. Then the total strain energy E_t can be calculated. We can obtain the analytic formula of E_t, then minimizing E_t calculate ϵ, but the obtained formula is very complex. From the numerical calculating, we find the same square reverse proportion relation between ϵ and ρ_0 which is expected by CET. The coefficient is slightly dependence on the helicity of tube, since it only depends on an average of $\cos^n\theta_{ij}$ in three bonds. Fig. 1 shows the radius dilation of some SWNTs expected by the expanded Lenosky model. It is very good in agreement with the characteristics ρ_0 square reverse proportion relation. As comparison, a first principles LDA calculation also be depicted in Fig. 1, which is well consistent with our results. Since the structure relaxation can be obviously affected by the energy term from bond length change, our obtained value of $\mathcal{E}_\prime$ from the relaxation is more exact than from the strain energy itself of tube. Therefore, our result shows the expanded Lenosky model which $\mathcal{E}_0$ is fitted from the force constant model of graphite can be well used in the studying of the carbon network deformations.

In our previous paper [14] using Tight-Binding (TB) approximation, we have successly calculated the strain energy of the bending tube, and simultaneously obtain the Young's modulus and the effective wall thickness of SWNT. It clarified the discrepancy on the wall thickness of single-layer structure [9–11]. The expanded Lenosky model can be used to study the same problem, too. Fig. 2 shows the strain energy per atom E_b of the (5,5) tube as a function of the bending radius R^2. The data follow quite well the expected behavior $E_b = E_r + \lambda/R^2$, where E_r is the rolling energy of tube. The fitting value of λ is about 185 eVÅ^2/atom, slightly larger than the TB result 173 eVÅ^2/atom [14] Fig. 3 shows λ is a linear function of ρ^2, $a^* + b^*\ \rho^2$, which is consistent with the relation expected by CET, $\lambda = \Omega\ Y\ b\ (\rho^2 + b^2/4)$, Where $\Omega = 2.62$ Å^2/atom is the occupied area per carbon atom in SWNTs, Y is Young's modulus, b is the wall effective thickness, and ρ is the radius of tube. The value of b^* is 16.2 eV/atom, slightly larger than the TB results 15.3. Since λ is far larger than a^*, it is difficult to exactly fit the value of a^* from the calculated data, due to the calculating errors. $a^* \approx 0.4$, if only using the data of (n, n) and $(n, 0)$ tube, but $a^* \approx 1.5$, if using the total data, where the unit of a^* is ${r_0}^2$eVÅ^2/atom . However, our obtained the value of b^* is insensistive to the selected data, and a^* is between 0.4 and 1.8, consist with the TB result 1.05 [14]. Fig. 4 shows the strain energy of straight tube $(1/R = 0)$ E_r is reverse proportion to the square of tube radius ρ, the coefficient is about 1.48 eVÅ^2/atom, good consistent with the TB calculation 1.44 eVÅ^2/atom. In previous TB approximation, since the unit cell of chiral tube is very large, calculating strain energy is an arduous work,

and the method include twelve parameters. We think the expanded Lenosky model can well be used to determine the carbon network structure.

In summary, our studies show the tube relaxation is inverse proportion to the square of the tube radius. The expanded Lenosky model which only include four parameters can well describe the deformation of the bending carbon nanotube. It may be a simple replacement of some complex methods in determining the equilibrium structure and the deformed energy of carbon networks.

The authors acknowledge the discussion with Dr. Haijun Zhou.

REFERENCES

[1] C. Dekker, Phys. Today, 22, (May. 1999).

[2] N. Hamada, S.Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992); R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. **60**,2204 (1992); J. M. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68**, 631, (1992).

[3] C. T. White, D. H. Robertson, and J. W. Mintmire, Phys. Rev. B **47**, 5485, (1993); H. Yorikawa and S. Muramatsu, Phys. Rev. B **52**, 2723, (1995).

[4] J. W. G. Wildöer, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, Nature (London) **391**, 59 (1998); T. W. Odom, J.-L. Huang, P. Kim, and C. M. Lieber, Nature (London) **391**, 62 (1998).

[5] M. S. Dresselhaus, Nature (London) **358**, 195 (1992).

[6] X. Blase, L. X. Benedict, E. L. Shirley, and S. G. Louie, Phys. Rev. Lett. **72**, 1878 (1994).

[7] Daniel S., E. Artacho, and J. M. Soler, **cond-mat/9811363**.

[8] J. Tersoff, Phys. Rev. B **46**, 15546 (1992).

[9] B. I. Yakobson, C. J. Brabec, and J. Bernholc, Phys. Rev. Lett. **76**, 2511 (1996).

[10] J. P. Lu, Phys. Rev. Lett. **79**, 1297 (1997).

[11] E. Hernández, C. Goze, P. Bernier, and A. Rubio, Phys. Rev. Lett. **80**, 4502 (1998).

[12] T. Lenosky, X. Gonze, M. Teter, and V. Elser, Nature (London) **355**, 333, (1992).

[13] Z.-C. Ou-Yang, Z.-B. Su, and C.-L. Wang, Phys. Rev. Lett. **78**, 4405 (1997).

[14] X. Zhou, J.-J. Zhou and Z.-C. Ou-Yang, **cond-mat/0001082**.

[15] J. Kurti, G. Kresse and H. Kuzmany Phys. Rev. B **58**, R8869, (1998).

[16] R. Al-Jishi and G. Dresselhaus, Phys. Rev. B **26**, 4514 (1982).

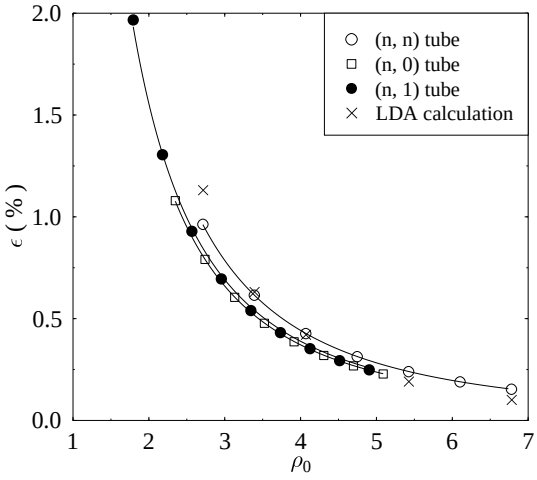

Fig. 1

FIG. 1. The radius dilation of SWNT ϵ versus the radius of tubes. The solid line drawn across the data corresponds to a least square fit to the $\frac{\alpha}{{\rho_0}^2}$ behaviors. The α values of the (n,n) $(n,0)$ and $(n,1)$ tubes are 0.071, 0.059 and 0.062 $\mathring{A}^2$, respectively, slightly depend on the helicity of SWNT. The results of LAD is from the fig. 1 (c) of ref. [7].

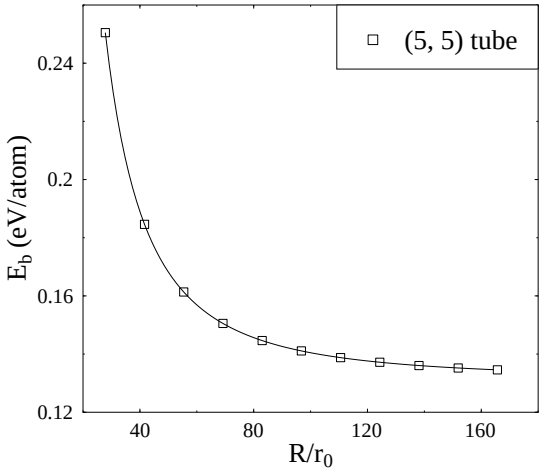

Fig. 2

FIG. 2. Strain energy per atom versus the bending radius R in (5,5) tube. The solid line is a fit to the $E_r + \lambda/R^2$, where E_r is the straight (5,5) tube strain energy. $\lambda = 92 \times 1.42^2$ eVÅ^2/atom. Here $r_0 = 1.42$ $\mathring{A}$, is the bond length of graphite.

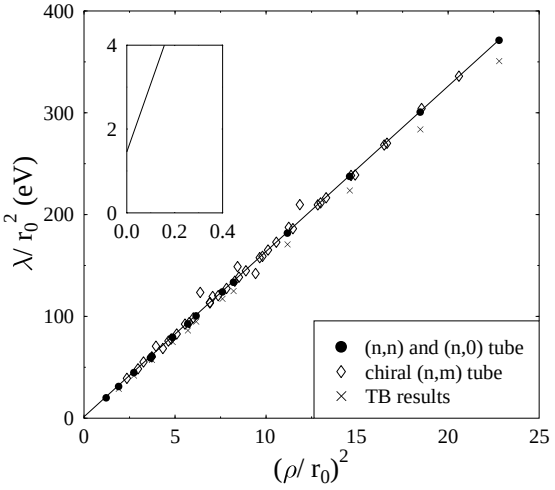

Fig. 3

FIG. 3. the value of λ of some (n,0) and (n,n) tubes and some chiral tubes. The solid line is a fit the all data to $a^* + b^*\rho^2$, $a^* \approx 1.5$ $r_0{}^2$ eVÅ^2/atom $b^* \approx 16.2$ eV. (TB results: $a^* \approx 1.05$, $b^* \approx 15.3$ eV in Ref. [14]). The inset shows the fitting solid line from all data nearby $\rho = 0$. To compare, we give the TB results, too.

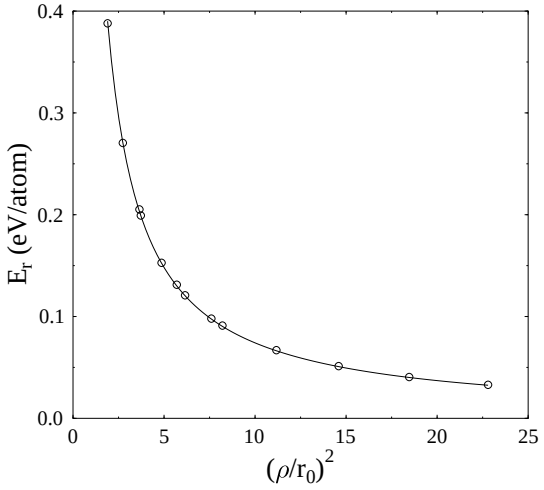

Fig. 4

FIG. 4. The strain energy per atom versus the radius of (n, n) and $(n, 0)$ tubes. The solid line drawn across the data corresponds to a least square fit to the $\frac{C}{\rho^2}$ behavior. $\mathcal{C} = 0.74 \cdot {r_0}^2 \approx 1.48$ eV$\mathrm{\AA}^2$/atom. $\mathcal{C}$ is independent on the helicity of tubes.